

PATENT SPECIFICATION

(11) 1 396 526

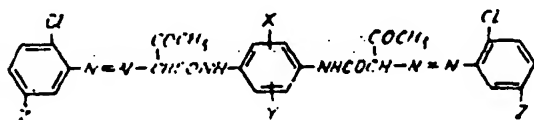
- (21) Application No. 41181/72 (22) Filed 5 Sept. 1972
 (31) Convention Application No. 13312/71 (32) Filed 10 Sept. 1971 in
 (33) Switzerland (CH)
 (44) Complete Specification published 4 June 1975
 (51) INT CL² C09B 33/14
 (52) Index at acceptance
 C4P 2G2B 2H10 2H12 2H13 2H3 2H9
 C3P 10C10 10D1A E2



(54) NEW DISAZO PIGMENTS AND PROCESS FOR THEIR MANUFACTURE AND USE

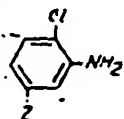
(71) We, CIBA-GEIGY AG, a Swiss body corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides, as new compounds, the disazo pigments of the formula:

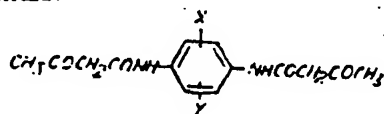


wherein X denotes hydrogen, halogen, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, trifluoromethyl, nitro, cyano amino-carbonyl, or alkoxy-carbonyl of 1 to 5 carbon atoms, Y denotes hydrogen, halogen, alkyl of 1 to 4 carbon atoms or trifluoromethyl and Z denotes chlorine, methyl or trifluoromethyl.

According to a feature of the invention these pigments are obtained by coupling a diazo compound or diazoamine compound of an amine of the formula:

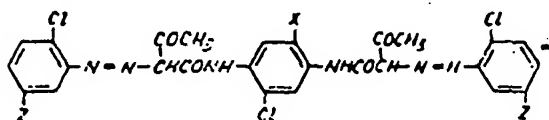


with a bis-acetoacetyl-p-phenylenediamine of the formula:



in the molar ratio of 2:1.

Disazo pigments of the formula:



[Price 33p]

wherein X denotes chlorine, methyl or methoxy, and Z denotes chlorine or trifluoromethyl are of particular interest.

Examples of diazo components are those derived from 2-chloro-5-trifluoromethylaniline, 2-chloro-5-methylaniline and especially 2,5-dichloroaniline.

The coupling components are obtained in a simple manner by the action of diketone or ethyl acetoacetate on the corresponding phenylenediamines such as, for example, 1,4-phenylenediamine, 2-chloro-1,4-phenylenediamine, 2-methyl-1,4-phenylenediamine, 2-methoxy-1,4-phenylenediamine, 2-ethoxy-1,4-phenylenediamine, 2-propoxy-1,4-phenylenediamine, 2-isopropoxy-1,4-phenylenediamine, 2-butoxy-1,4-phenylenediamine, 2-nitro-1,4-phenylenediamine, -cyano-1,4-phenylenediamine, 2-methoxycarbonyl-1,4-phenylenediamine, 2-ethoxycarbonyl-1,4-phenylenediamine, 2-trifluoromethyl-1,4-phenylenediamine, 2-aminocarbonyl-1,4-phenylenediamine, 2,5-dichloro-1,4-phenylenediamine, 2,5-dibromo-1,4-phenylenediamine, 2,5-dimethyl-1,4-phenylenediamine, 2,5-bis-trifluoromethyl-1,4-phenylenediamine, 2-chloro-5-methyl-1,4-phenylenediamine, 2-chloro-5-methoxy-1,4-phenylenediamine, 2-chloro-5-ethoxy-1,4-phenylenediamine, 2-methyl-5-methoxy-1,4-phenylenediamine and 2-methyl-5-ethoxy-1,4-phenylenediamine.

The coupling preferably takes place in a weakly acid medium, appropriately in the presence of customary agents which assist coupling. Suitable such agents include dispersing agents, for example aralkylsulphonates, such as dodecylbenzenesulphonate, or 1,1'-dinaphthylmethane-2,2'-disulphonic acid or polycondensation products of alkylene oxides. The dispersion of the coupling component can also advantageously contain protective colloids, for example methyl-cellulose or minor amounts of inert solvents which are sparingly soluble or insoluble in water, for example monally halo-

generated or nitrated aromatic hydrocarbons, such as benzene, toluene, xylene, chlorobenzene, dichlorobenzene or nitrobenzene, as well as aliphatic halogenated hydrocarbons, such as, for example, carbon tetrachloride or trichloroethylene, and also water-miscible organic solvents such as acetone, methyl ethyl ketone, methanol, ethanol or isopropanol.

The coupling can also advantageously be carried out by continuously combining an acid solution of the diazonium salt with an alkaline solution of the coupling component in a mixing nozzle, whereupon immediate coupling of the components takes place. Care must be taken that the diazo component and the coupling component are present in equimolecular amounts in the mixing nozzle and it proves advantageous to use a slight excess of the diazo component. This is most simply effected by controlling the pH value of the liquid in the mixing nozzle. Vigorous intermixing of the two solutions must also be ensured in the mixing nozzle. The resulting dyestuff dispersion is continuously withdrawn from the mixing nozzle and the dyestuff is removed by filtration.

The coupling can also be carried out by heating a diazoamino compound of the amine used as the diazo component with the bisacetoacetyl- β -phenylene diamine in an organic solvent, or in an aqueous-organic solvent, preferably in the presence of an acid.

The diazoamino compounds used in the process are obtained according to known processes by coupling a diazonium salt of the amine which serves as the diazo component with a primary or preferably with a secondary amine. The most diverse amines are suitable for this purpose, for example aliphatic amines, such as methylamine, ethylamine, ethanolamine, propylamine, butylamine, hexylamine and especially dimethylamine, diethylamine, diethanolamine, methyl-ethanolamine, dipropylamine or dibutylamine, aminoacetic acid, methylaminoacetic acid, butylaminoacetic acid, aminoethanesulphonic acid, methylaminoethanesulphonic acid, guanylethanesulphonic acid, β -aminoethylsulphuric acid, aliphatic amines such as cyclohexylamine, N-methylcyclohexylamine and dicyclohexylamine, aromatic amines such as 4-aminobenzoic acid, sulphanilic acid, 4-sulpho-2-aminobenzoic acid, (4-sulphophenyl)-guanidine, 4-N-methylaminobenzoic acid, 4-ethylaminobenzoic acid, 1-aminonaphthalenesulphonic acid, 1-aminonaphthalene-2,4-disulphonic acid, heterocyclic amines such as piperidine, morpholine, pyrrolidine and dihydroindole and finally also sodium cyanamide or dicyandiamide.

As a rule, the diazoamino compounds obtained are sparingly soluble in cold water and can be separated from the reaction medium in a crystalline form, if necessary after salting out. In many cases, the moist press cakes can be used for the further reaction. In some cases

it can prove desirable to dehydrate the diazoamides by vacuum drying prior to the reaction or to remove the water by azeotropic distillation after suspending the moist press cake in a solvent.

The coupling of the diazoamino compound with the bis-acetoacetyl- β -phenylene diamine is carried out in an organic solvent, for example chlorobenzene, *o*-dichlorobenzene, nitrobenzene, pyridine, ethylene glycol, ethylene glycol monomethyl ether or monoethyl ether, dimethylformamide, N-methylpyrrolidone, formic acid or acetic acid. If solvents which are miscible with water are employed, it is not necessary to use the diazoamino compound in the anhydrous form. For example, the water-moist filter cakes can be used. The splitting of the diazoamino compound which precedes the coupling is carried out in an acid medium. If neutral solvents are used the addition of an acid, for example hydrogen chloride, sulphuric acid, formic acid, acetic acid, chloroacetic acid or propionic acid is necessary.

The coupling is appropriately carried out with warming, preferably at temperatures of between -80° and 180°C, and in general takes place very rapidly and completely.

As the result of their insolubility, the pigments obtained can be isolated from the reaction mixtures by filtration. It proves advantageous to subject the resulting pigments to an after-treatment with an organic solvent which preferably boils above 100°C. Particularly suitable solvents prove to be benzenes substituted by halogen atoms or alkyl or nitro groups, such as xylenes, chlorobenzene, *o*-dichlorobenzene or nitrobenzene, and pyridine bases, such as pyridine, picoline or quinoline, and also ketones, such as cyclohexanone, ethers, such as ethylene glycol monomethyl ether or monoethyl ether, amides, such as dimethylformamide or N-methylpyrrolidone, and tetrahydrothiophene dioxide.

The after-treatment is preferably carried out by heating the pigment, in the solvent, to 100—150°C, whereupon in many cases an increase in the particle size occurs, which has a favourable effect on the fastness of the resulting pigments to light and to migration.

Finally, the coupling can also be effected by suspending the amine to be diazotised, together with the coupling component, in the molar ratio of 2:1, in an organic solvent and treating it with a diazotising agent, especially an ester of nitrous acid, such as methyl nitrate, ethyl nitrite, butyl nitrite, amyl nitrite or octyl nitrite.

The new pigments in a finely divided form can be used for pigmenting high molecular weight organic material, for example cellulose ethers and cellulose esters, polyamides or polyurethanes or polyesters, acetylcellulose, nitrocellulose, natural resins or synthetic resins, such as polymerisation resins or condensation resins, for example aminoplasts, especially

urea-formaldehyde and melamine-formaldehyde resins, alkyd resins, phenoplasts, polycarbonates, polyolefines, such as polystyrene, polyvinyl chloride, polyethylene, polypropylene, polyacrylonitrile, polyacrylic acid esters, rubber, casein, silicone and silicone resins, individually or as mixtures.

It does not matter whether the high molecular weight compounds mentioned are in the form of plastic masses or melts or in the form of spinning solutions, lacquers, paints or printing inks. Depending on the end use it may be advantageous to employ the new pigments as toners or in the form of preparations. The preparations can for example contain, in addition to the pure pigment, natural resins, for example abietic acid or its esters, ethylcellulose, cellulose acetobutyrate, alkaline earth metal salts of higher fatty acids, fatty amines, for example stearylamine or rosin amine, vinyl chloride-vinyl acetate copolymers, polyacrylonitrile or polyterpene resins or water-soluble dyestuffs, for example dyestuff-sulphonic acids or their alkaline earth metal salts.

In the examples which follow the parts, unless otherwise stated, denote parts by weight, the percentages denote percentages by weight and the temperatures are given in degrees centigrade. The relationship of parts by weight to parts by volume is the same as that of the kilogram to the litre.

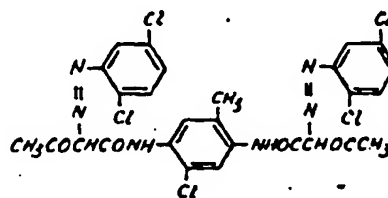
As compared to the benzidine yellow pigments, the pigments of the invention have the advantage that benzidine, which is injurious to health, is not required as an intermediate. As compared to the dyestuffs of U.S. Patent 1,99,438, the pigments according to the invention are distinguished by better fastness to migration.

Example 1.

14.35 parts of 2,5-dichloroaniline in 300 parts by volume of glacial acetic acid are stirred with 25 parts by volume of concentrated hydrochloric acid, whereupon the hydrochloride of the base forms. The mixture is then cooled to -5°C by adding 300 parts of ice and is diazotised by adding 24 parts by volume of 4 N sodium nitrite. The yellow diazo solution is stirred at $0-5^{\circ}\text{C}$ until only traces of nitrous acid are still detectable. The diazo solution is then clarified by filtration, with the addition of a little decolourising charcoal. The filtrate is brought to pH 4 by adding 40 parts of anhydrous sodium acetate.

At the same time, 13.0 parts of 2-methyl-5-chloro-1,4-bisacetoacetylanilino benzene are dissolved in 800 parts of water and 12 parts by volume of 40% strength sodium hydroxide solution and 5 parts of n-butyl sulphuric le-

ate are added. This solution is clarified by filtration, using 0.5 part of decolourising charcoal, and is then added dropwise over the course of 1-1½ hours, to the diazo solution, whilst stirring well. In the course of the addition the temperature of the reaction mixture rises to $15-20^{\circ}\text{C}$. After completion of the dropwise addition, diazo compound is no longer detectable in the mixture. The mixture is stirred for one hour at room temperature, then warmed to $80-85^{\circ}\text{C}$ over the course of 1 hour and filtered hot, and the product is washed with hot water until free of salt. After drying in vacuo at $95-100^{\circ}\text{C}$, 19.9 parts of a yellow dyestuff of the formula



are obtained.

19.9 parts of the pigment thus obtained are stirred with 600 parts by volume of ethylene glycol monomethyl ether for 8 hours at $145-150^{\circ}\text{C}$. In the course thereof, the pigment assumes a uniformly crystalline form. Fine yellow particles of length $1\ \mu$ are detectable under the microscope. The product is filtered off at 140°C and washed with boiling ethylene glycol monomethyl ether until the filtrate issues colourless, the ethylene glycol monomethyl ether is then displaced by dimethylformamide and finally the product is again washed with ethanol. After drying, 14.0 parts of a luminous yellow pigment are obtained. It dyes plastics such as PVC (polyvinyl chloride) in greenish-tinged yellow shades of excellent fastness to migration. The treatment in the organic solvent can also be carried out directly on the moist filter cake without prior drying. Thus it is possible to stir the moist press cake in picoline at $100-120^{\circ}\text{C}$ and to filter off the product and wash it with methanol and subsequently with dilute hydrochloric acid, or to stir the moist press cake in chlorobenzene, o-dichlorobenzene or nitrobenzene, free it of water by azeotropic distillation and then work up the product as described above.

The table which follows describes further pigments which are obtained by coupling the diazotised bases of column I with the bis-acetoacetic acid arylides of the diamines of column II. Column III indicates the colour shade of the PVC film coloured with 0.2% of these pigments.

1,396,526

TABLE I

Example N.	Diazo base	Bis-acetoacetyl compound of the diamine	0.2% colouration in PVC
2	2,5-Dichloro-aniline	1,4-Phenylenediamine	light yellow
3	2,5-Dichloro-aniline	2-Chloro-1,4-phenylenediamine	yellow
4	2,5-Dichloro-aniline	2-Methyl-1,4-phenylenediamine	yellow
5	2,5-Dichloro-aniline	2-Methoxy-1,4-phenylenediamine	yellow
6	2,5-Dichloro-aniline	2-Ethoxy-1,4-phenylenediamine	yellow
7	2,5-Dichloro-aniline	2,5-Dichloro-1,4-phenylenediamine	yellow
8	2,5-Dichloro-aniline	2-Methoxy-5-chloro-1,4-phenylenediamine	yellow
9	2,5-Dichloro-aniline	2-Ethoxy-5-chloro-1,4-phenylenediamine	yellow
10	2,5-Dichloro-aniline	2,5-Dimethyl-1,4-phenylenediamine	yellow
11	2,5-Dichloro-aniline	2-Methoxy-5-methyl-1,4-phenylenediamine	orange yellow
12	2-Chloro-5-trifluoromethyl-aniline	1,4-Phenylenediamine	light yellow
13	2-Chloro-5-trifluoromethyl-aniline	2-Chloro-1,4-phenylenediamine	light yellow
14	2-Chloro-5-trifluoromethyl-aniline	2-Bromo-1,4-phenylenediamine	light yellow
15	2-Chloro-5-trifluoromethyl-aniline	2-Trifluoromethyl-1,4-phenylenediamine	yellow
16	2-Chloro-5-trifluoromethyl-aniline	2-Cyano-1,4-phenylenediamine	yellow
17	2-Chloro-5-trifluoromethyl-aniline	2-Nitro-1,4-phenylenediamine	yellow

1,396,526

TABLE I (Continued)

Example No.	Diazo base	Bis-acetoacetyl compound of the diamine	0.2% colouration in PVC
18	2-Chloro-5-trifluoromethyl-aniline	2-Methyl-1,4-phenylenediamine	yellow
19	2-Chloro-5-trifluoromethyl-aniline	2-Methoxy-1,4-phenylenediamine	yellow
20	2-Chloro-5-trifluoromethyl-aniline	2-Ethoxy-1,4-phenylenediamine	yellow
21	2-Chloro-5-trifluoromethyl-aniline	2,5-Dichloro-1,4-phenylenediamine	greenish-tinged yellow
22	2-Chloro-5-trifluoromethyl-aniline	2,3-Dichloro-1,4-phenylenediamine	greenish-tinged yellow
23	2-Chloro-5-trifluoromethyl-aniline	2,6-Dichloro-1,4-phenylenediamine	greenish-tinged yellow
24	2-Chloro-5-trifluoromethyl-aniline	2,5-Dibromo-1,4-phenylenediamine	greenish-tinged yellow
25	2-Chloro-5-trifluoromethyl-aniline	2,5-Bis-trifluoromethyl-1,4-phenylenediamine	yellow
26	2-Chloro-5-trifluoromethyl-aniline	2-Chloro-5-methoxy-1,4-phenylenediamine	reddish-tinged yellow
27	2-Chloro-5-trifluoromethyl-aniline	2-Chloro-5-ethoxy-1,4-phenylenediamine	yellow
28	2-Chloro-5-trifluoromethyl-aniline	2,5-Dimethyl-1,4-phenylenediamine	yellow
29	2-Chloro-5-trifluoromethyl-aniline	2-Methoxy-5-methyl-1,4-phenylenediamine	yellow
30	2-Chloro-5-trifluoromethyl-aniline	2-Chloro-5-methyl-1,4-phenylenediamine	yellow
31	2-Chloro-5-methyl-aniline	1,4-Phenylenediamine	neutral yellow
32	2-Chloro-5-methyl-aniline	2-Chloro-1,4-phenylenediamine	greenish-tinged yellow
33	2-Chloro-5-methyl-aniline	2-Methyl-1,4-phenylenediamine	yellow
34	2-Chloro-5-methyl-aniline	2-Methyl-5-chloro-1,4-phenylenediamine	yellow
35	2-Chloro-5-methyl-aniline	2-Methoxy-5-chloro-1,4-phenylenediamine	yellow

Example 36.

14.35 parts of 2,5-dichloroaniline and 13 parts of 2-methyl-5-chloro-1,4-bisacetoacetylaminobenzene are suspended in a mixture of 400 parts by volume of cellosolve and 100 parts by volume of glacial acetic acid. Thereafter the suspension is warmed to 90–100°C and stirred until complete solution has occurred. The mixture is then stirred until it has cooled to room temperature. 60 parts by volume of butyl nitrite, as a 2 N solution in o-dichlorobenzene, are now slowly added to the fine suspension obtained. Hereupon a yellowish-tinged fine suspension is immediately produced and the temperature slowly rises to 35°C. After completion of the dropwise addition the mixture is stirred for a further hour at room temperature, as a result of which a yellow suspension is ultimately obtained. This is then warmed to 80–90°C and the mixture is stirred for a further 15 hours at this temperature. The pigment thus attains a consistent form and fine yellow amorphous aggregates of size 5–10 μ are detectable under the microscope.

Thereafter the pigment is filtered off at 80°C and washed with hot ethylene glycol monomethyl ether until the filtrate issues colourless. The filter residue is then rinsed with a little hot dimethylformamide and ethanol and dried in vacuo at 70°C. 18.4 parts of a yellow pigment are thus obtained.

15.4 parts of this pigment are now stirred in 450 parts by volume of dimethylformamide to improve its form. Thereafter the mixture is warmed to 160–170°C and stirred for a further 15 hours at this temperature. This produces a fine yellow suspension, and very fine yellow particles of size 1–3 μ can be seen under the microscope.

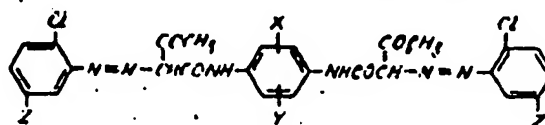
The product is then filtered off at 150°C and washed with boiling dimethylformamide until the filtrate is only slightly coloured. The filter residue is then rinsed with boiling ethylene glycol monomethyl ether until the filtrate issues colourless. The ethylene glycol monomethyl ether is then displaced with a little ethanol and the filter residue is dried in vacuo at 70°C. The yield is 12.1 parts and the yellow colour of the pigment appears somewhat more luminous than before the treatment.

Example 37.

65 parts of stabilised polyvinyl chloride, 35 parts of dioctyl phthalate and 0.2 part of the dyestuff obtained according to Example 1 are stirred together and then worked by milling on a two bowl calender for 7 minutes at 140°C. A yellow-coloured film of very good fastness to light and to migration is obtained.

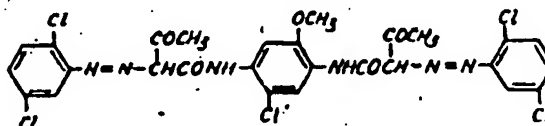
WHAT WE CLAIM IS:—

1. Disazo pigments of the formula:

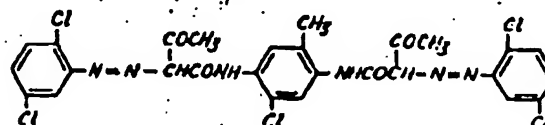


wherein X denotes hydrogen, halogen, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, trifluoromethyl, nitro, cyano, aminocarbonyl, or alkoxy carbonyl of 1 to 5 carbon atoms, Y denotes hydrogen, halogen, alkyl of 1 to 4 carbon atoms or trifluoromethyl, and Z denotes chlorine, methyl or trifluoromethyl.

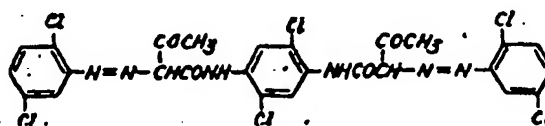
2. A disazo pigment according to claim 1, of the formula



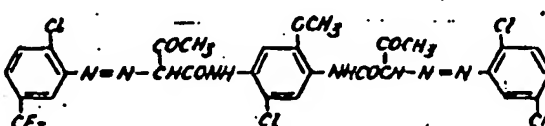
3. A disazo pigment according to claim 1, of the formula



4. A disazo pigment according to claim 1, of the formula



5. A disazo pigment according to claim 1, of the formula



6. Process for the manufacture of a disazo pigment as claimed in claim 1, which comprises coupling a diazo or diazoamino compound of an amine of the formula

